Measurement and Manipulation of Defects in Gallium Oxide

Senior Honors Thesis

Presented in Partial Fulfillment of the Requirements for
Graduation with Honors and Distinction in the
College of Engineering of The Ohio State University

By

Shreyas Muralidharan

* * * * *

The Ohio State University

2019

Honors Thesis Committee:

Dr. Leonard Brillson, Adviser

Dr. Robert Perry

ABSTRACT

Gallium Oxide (Ga2O3) is a material of wide interest in power devices due to its wide bandgap. However, defects present in the lattice present problems due to the obstruction of charge transfer through the material, which is essential for the operation of devices such as transistors. The nature of several defect states in Gallium Oxide was determined through various experimental methods such as Depth Resolved Cathodoluminescence Spectroscopy (DRCLS) and Surface Photovoltage Spectroscopy (SPS). Treatment methods served to determine the nature of oxygen vacancies, and the initial concentration of these defects was determined. The effect of treatment methods such as neutron irradiation on these defect states was also investigated.

ACKNOWLEDGEMENTS

Thank you to Professor Leonard Brillson, for his never-ending support and wealth of knowledge that has been critical to my undergraduate research and academic success, and to The College of Engineering for a scholarship for the pursuit of this research. Particular thanks to Hantian Gao, with whom most of this work was done, and the other wonderful members of the research group who gave me encouragement and aid. My heartfelt thanks to my family and friends without whose support none of this would have been possible.

CHAPTER 1

INTRODUCTION

The increasing growth in the technology sector has led to an explosion in the development of innovative ideas including alternative energy vehicles and the need to develop concepts such as alternative energy further. These products require electronics that can work at high power, yet with small footprints and high efficiency. Material limitations prohibit the use of traditional electronic technologies for these applications. Therefore, it is critical that materials research and the discovery of new materials for these applications is done. A breakthrough in the area of electronic materials can usher in many of these technologies and make them more viable.

A host of materials have been used to create these higher power devices that could promise better performance for these applications. Materials such as silicon carbide (SiC) and gallium nitride(GaN) promise many of these advantages but are quite expensive compared to gallium oxide when it is grown using current methods. These materials have been extensively researched, and their weaknesses and strengths have largely been characterized. Gallium oxide is

still a relatively young material, and there are several directions of research that should be explored before it is mature enough to create devices and applications out of. The material has great potential, but there are many issues that must be resolved before it can become a staple in modern day electronics.

Semiconductor Background

A semiconductor material is a material that has an electrical conductivity between a metal and insulator. However, their electrical properties can be drastically altered by introducing impurities into the material, in a process called doping. Doping involves placing different atoms into the lattice, creating an excess of electrons or holes in a region. While devices can be made with only p(holes are the majority carrier) or n(electrons are the majority carrier) doping, most modern device structures require the use of both p and n doping to create high performance devices.

Another special feature of semiconductor materials is the presence of a bandgap, or a region of forbidden energies, between two regions of allowed energies, known as the conduction and valence band. Between these two states can lie defect states, also known as trap states. The presence of these defect states is detrimental to device performance. On the next page is a diagram of a possible semiconductor material with a trap state in the middle of the bandgap. These recombination events are essential to the measurement process described in this thesis, and make up the majority of the data taken.

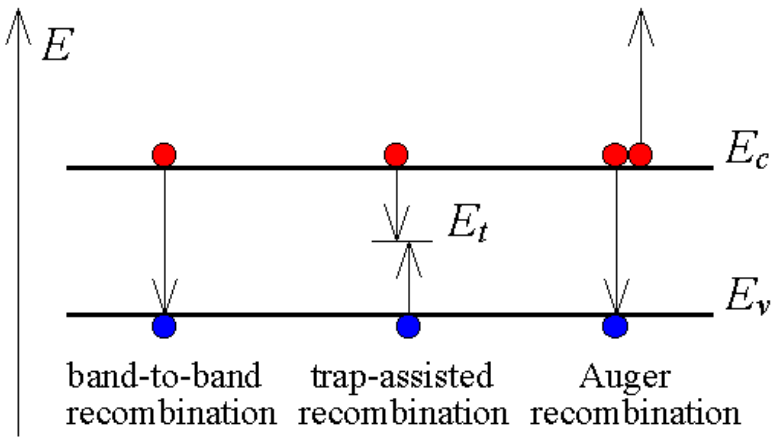

Figure 1: The conduction and valence band with different types of recombination shown

Material Background and Information

Gallium Oxide (Ga_2O_3) is a compound semiconductor material with potential for use in several different applications. Most notable are devices used in high voltage and high-power systems for electric cars and alternative energy. Several reasons point to using Ga_2O_3, but its ultra-wide bandgap is one of its primary strengths. Compared to the 2.06 to 3.03 eV of SiC, and the 3.4 eV of GaN, the 4.9 eV[1] band gap of Ga_2O_3 is one of the primary reasons for its success in these high power applications. This larger band gap allows the material to be more resistant to voltage breakdown, and therefore devices made out of these materials can be operated at higher frequencies, voltages, and temperatures.

Gallium oxide can also be acquired and made relatively easily and at a low cost. A process widespread in the silicon world, the Czochralski method, has been demonstrated to have worked with gallium oxide, and other growth methods such as pulsed layer deposition have resulted in the growth of high quality films. However, there are also problems with the material. Currently,

devices created in this material are unipolar. For device structures to be optimally effective in gallium oxide, the properties of the material must be tunable, with the introduction of both electron donors and acceptors. Current work focuses on investigating the properties of these materials with other extrinsic dopants, as well as the tunability of point defects in the material.

The Electronic Materials and Nanostructures Laboratory at Ohio State has been conducting research on this material for the past year. This has involved a study of gallium oxide samples synthesized using different growth methods, and performing various surface treatment methods to ascertain the nature of the intrinsic defects present in the material. This thesis describes the work done by Hantian Gao, Nick Pronin, and I from the Ohio State EMNL group.

The remainder of this thesis describes the measurement techniques used, the results obtained, and future work that will lead to the successful application of this material.

CHAPTER 2

MEASUREMENT TECHNIQUES

A few major techniques contributed to the data and results for this project. These include DRCLS(Depth- Resolved Cathodoluminescence Spectroscopy), SPS(Surface Photovoltage Spectroscopy), and tSPS(Transient Surface Photovoltage Spectroscopy). The combination of these techniques are able to provide characteristics of the defects present in the material. These techniques will be described in further detail in this section.

2.1 Depth-Resolved Cathodoluminescence Spectroscopy(DRCLS)

Cathodoluminescence spectroscopy involves shooting an electron beam of varying energies at a sample. The electrons impacting on this material results in a recombination event between a hole and an electron, resulting in luminescence. In addition, band-to-band transitions can also be detected, which is useful for observing the bandgap of a material.

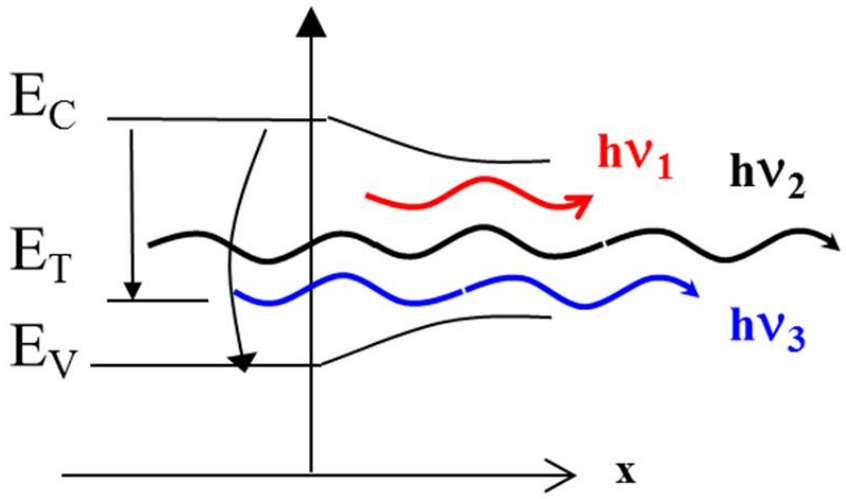

Figure 2: Visual Diagram of Transitions Present in Cathodoluminescence

Further relevant for the study of defects in materials is the ability to detect transitions to and from defect states in the middle of the bandgap. The characteristic light that comes from each of these transitions can be isolated through statistical analysis of the spectra. This technique is particularly

useful for the study of defects, because each mid-gap state will have a distinct energy and therefore can be identified by looking at the spectra. For example, the figure below shows an example spectra.

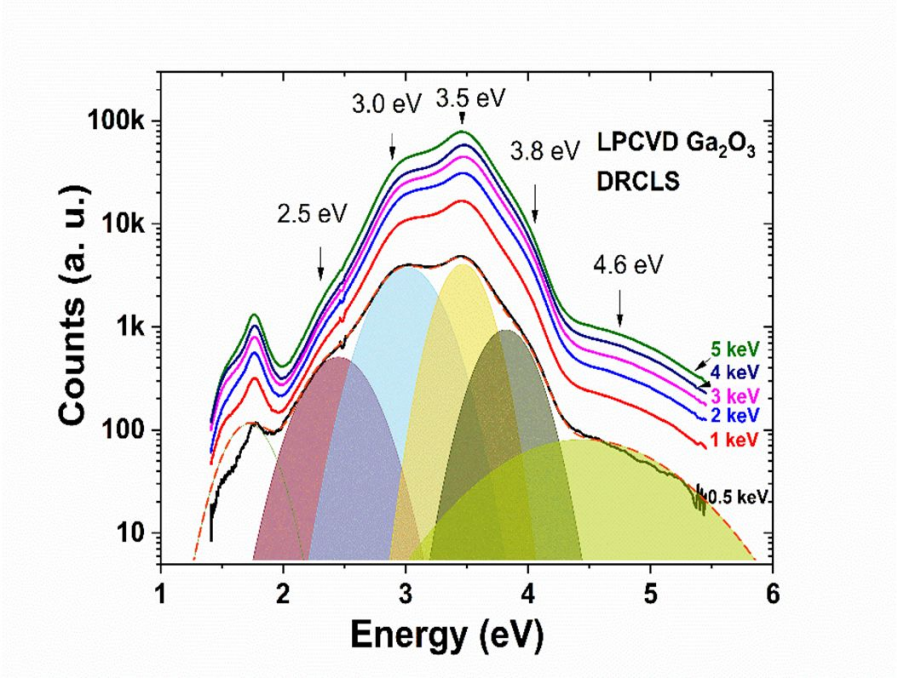

Figure 3: DRCLS Spectra of LPCVD grown Gallium Oxide

Present in this figure are clear peaks in which the energy levels of 2.5eV, 3.0 eV, 3.5eV, 3.8eV, and 4.6eV have been identified as a feature. Further analysis of this spectra will be presented later.

The idea of cathodoluminescence spectroscopy(CLS) combined with keeping a constant power in the electrons but varying the voltage used to accelerate the electron source leads to an extremely powerful tool called Depth Resolved CLS[3]. The figure below gives a diagram of the

system used to perform this technique. A chamber of this type was used to take the majority of the data presented in this thesis.

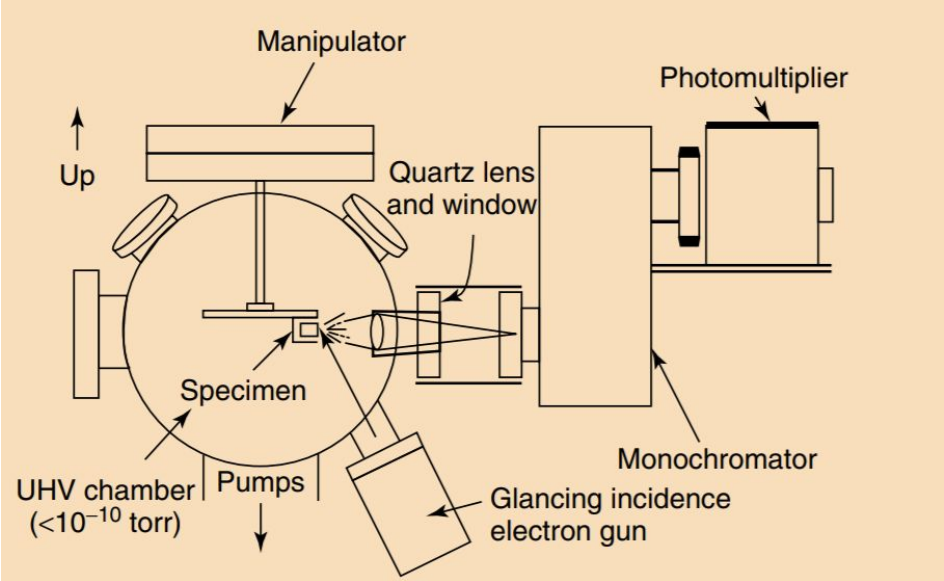

Figure 4: Schematic of CLS Equipment

The ability to take spectra with depth dependence leads to possibilities such as investigating defect states present only deep in the sample, or investigate the presence of a defect throughout the sample. The combination of this technique with surface sensitive treatment techniques can lead to the investigation of the nature of certain defects, an idea that is explored later.

2.2 Surface Photovoltage Spectroscopy(SPS)

Surface photovoltage spectroscopy (SPS) involves varying the voltage across a capacitor probe that is held very close to the sample. This induces a displacement current due to the difference in voltage between the probe and the sample. This technique can measure the bending in the bands of the sample, due to the movement and presence of excess charge carriers. When

light is shone upon the sample in the form of a laser in a specific energy, the process of photo-population or photo-depopulation of the states in the valence or conduction band can be detected as a voltage difference in the probe. The figure below shows a schematic of the experimental apparatus, as well as the photo-population and de-population states.

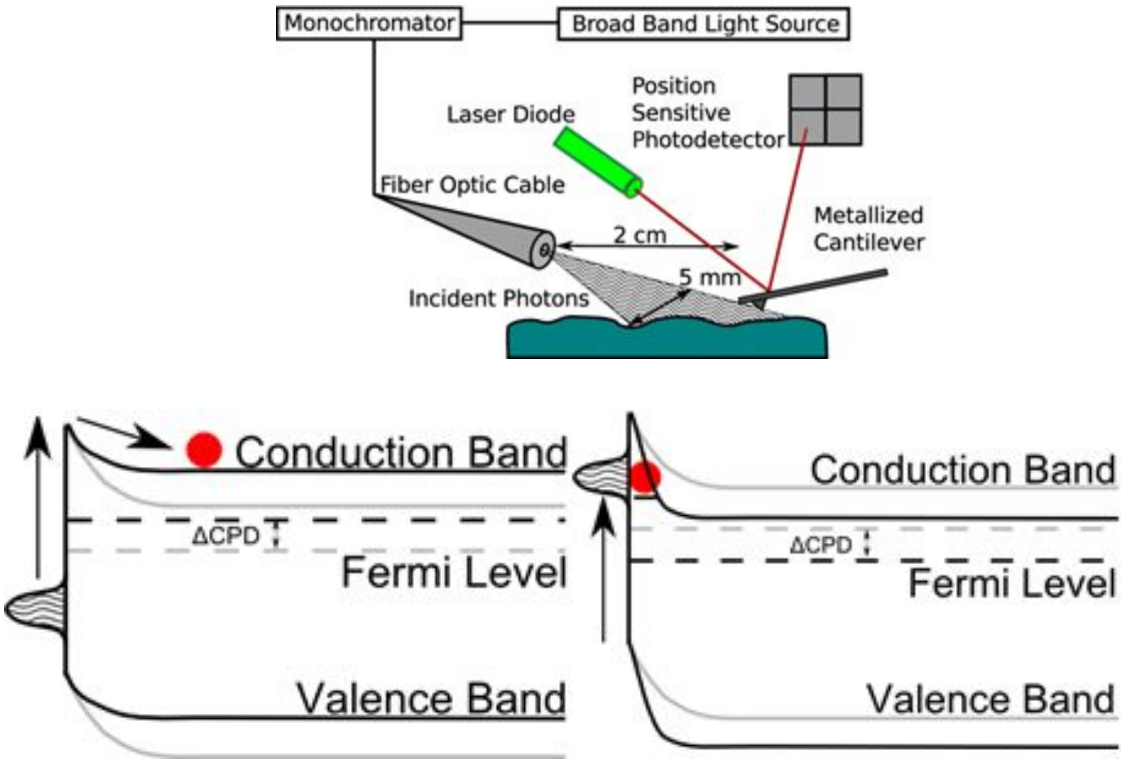

Figure 5: Experimental setup of SPS, and band bending as a result of the change in states

The changes in the voltage detected by the probe can be detected, leading to the detection of mid-gap states, and their approximate energy levels.

2.3 Transient SPS

Transient SPS[4] is an extension of the SPS technique. As the name might suggest, the technique involves shooting a given energy of light at the sample, and observing the resultant voltage signal over time. This technique is useful because it can give an estimate of the concentration of a defect state at a given energy, information that can subsequently be used to evaluate the effectiveness of a given surface treatment. A possible spectra is shown below, marked with the times at which the light is turned on and off.

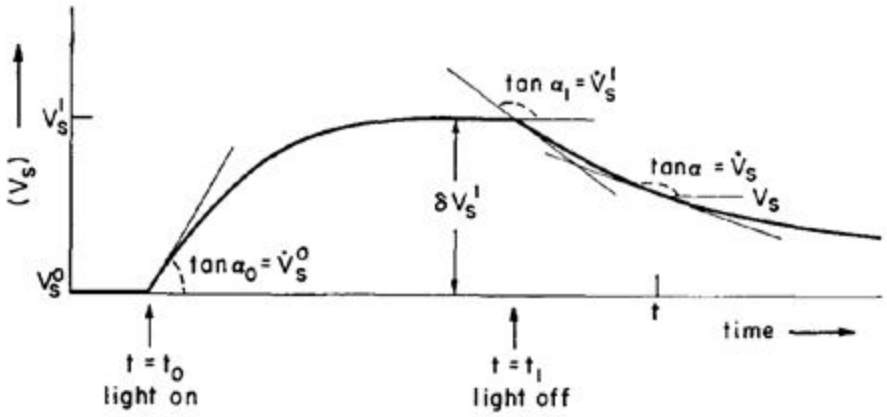

Figure 6: Possible T-SPS Spectra

CHAPTER 3

RESULTS

The study of this material was accomplished through investigating the properties of several samples grown with different methods, including PLD(Pulsed Laser Deposition) and LPVCD(Low Pressure Chemical Vapor Deposition), and MBE(Molecular Beam Epitaxy). The data presented will focus mainly on treatments and results from samples synthesized using these three growth methods.

Identification of Oxygen Vacancy

The figure below shows a DRCLS spectra of an LPCVD sample with no treatments. Notable features include peaks, signifying defect states or trap states in the material, at 2.5 eV, 3.0 eV, and 3.5 eV. The majority of the work done in the early part of this project was the identification of these peaks.

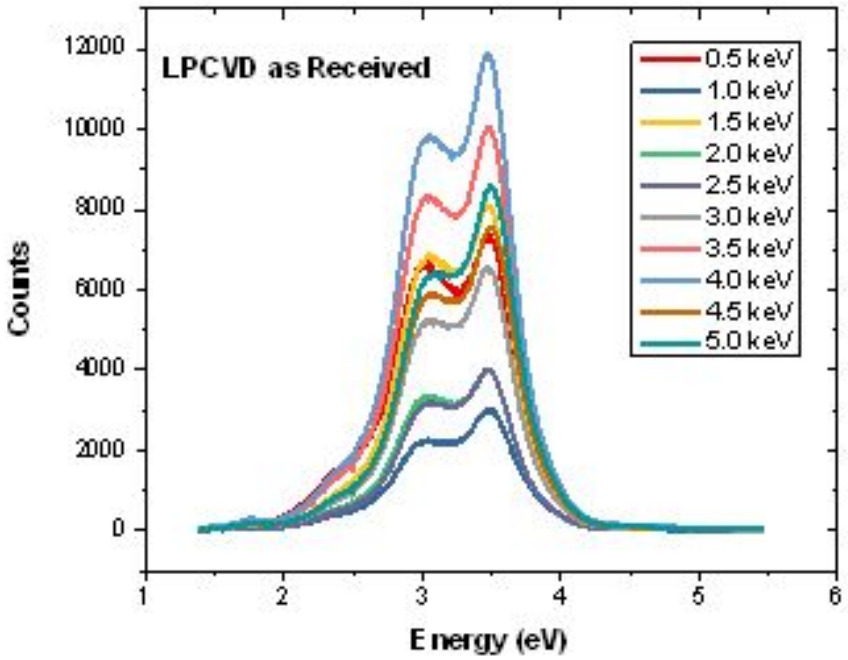

Figure 7: DRCL Spectra of unmodified LPCVD gallium oxide sample

A remote oxygen plasma(ROP) was used on this sample. Oxygen plasma involves flooding the surface of the sample with oxygen atoms, and is thought to passivate, or reduce a defect type known as an oxygen vacancy, a missing oxygen atom in the lattice. The sample was held in an ultrahigh vacuum (UHV) chamber with constant helium (He) and oxygen (O2) flow

with flow speed of 5.6 and 2.6 sccm respectively. A RF power source was used to trigger the oxygen plasma 15 cm above the sample surface, with a forward bias of 40V and a reflective bias of 1 V. The figure on the next page shows the post ROP DRCLS spectra of the sample.

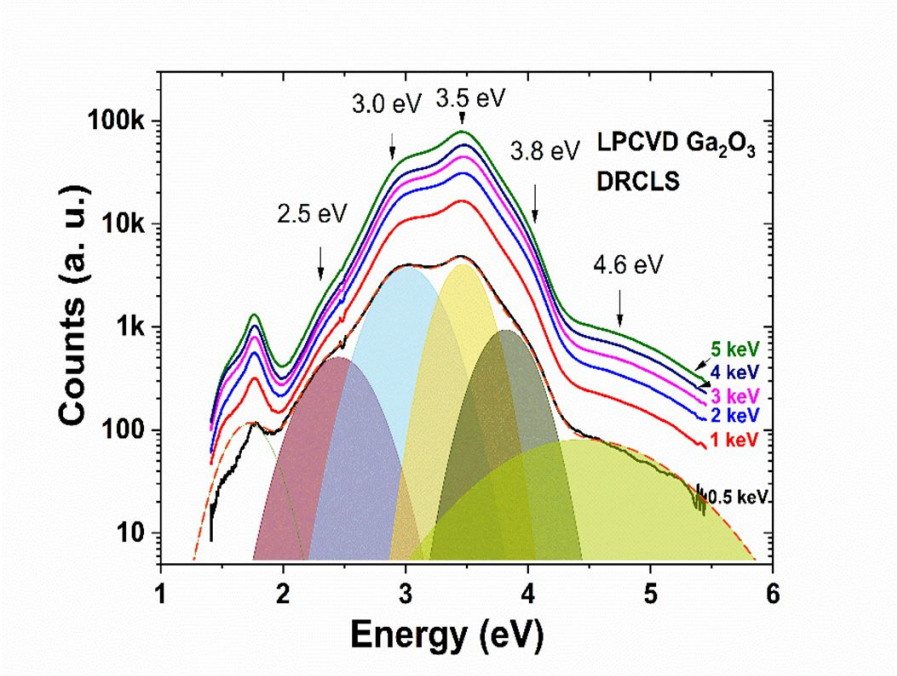

Figure 8: DRCL Spectra of LPCVD Ga_2O_3 after 1.75 hour ROP[2]

Shown in this figure are also deconvolved peak areas in which Gaussian fits were fit to the spectra to ascertain relative intensities of each of these peaks. These peak areas were compared to each other by normalizing their intensities, or dividing by the peak area of the bandgap, which is shown at 4.6 eV. This gives a depth profile of a given peak, as the bandgap peak area should be relatively constant, as it is a feature consistent throughout the sample. The figure below shows this depth profile.

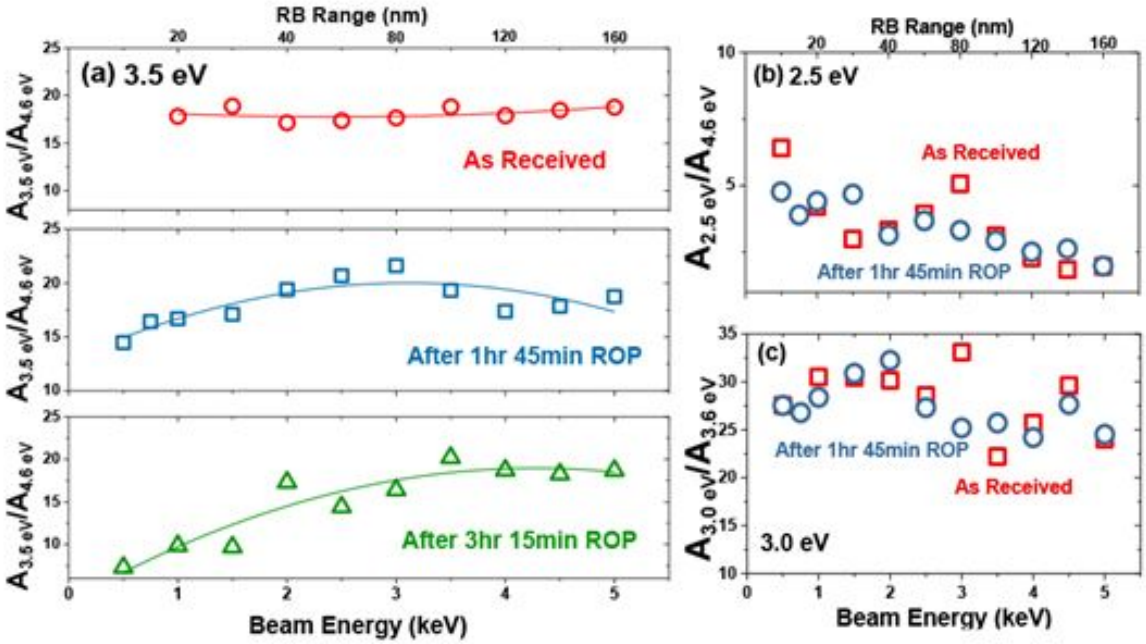

Figure 9: Depth Profiles of 3.5 eV peak area versus beam energy(analogous to depth into sample). Notice the decrease in normalized peak area near the surface after ROP treatment.

In this figure, it can be seen that post ROP, the relative peak area of the 3.5 eV feature decreases near the surface. CASINO Monte Carlo simulation software was used to estimate the depth of the beam for a given beam energy. In addition, it can also be seen that the relative peak areas for the 2.5 eV and the 3.0 eV features do not exhibit as much of a change from the ROP treatment. This suggests that the 3.5 eV feature is related to oxygen vacancies, as vacancies near the surface of the sample are filled by oxygen atoms entering the lattice through the surface.

Neutron Irradiation Studies

Neutron irradiation[5] was done at the Ohio State University Research Reactor to identify defect features associated with gallium vacancies. Past work has identified defect features as gallium vacancies. The figure below shows the CL Spectra obtained before and after irradiation. The crystal was held for 3 hours in the central irradiation position of the reactor where the total flux was ~2.3×10^{13} neutrons cm^{-2} s^{-1} and the thermal flux was ~1.4×10^{13} neutrons cm^{-2} s^{-1} with temperature estimated not to exceed 150°C.

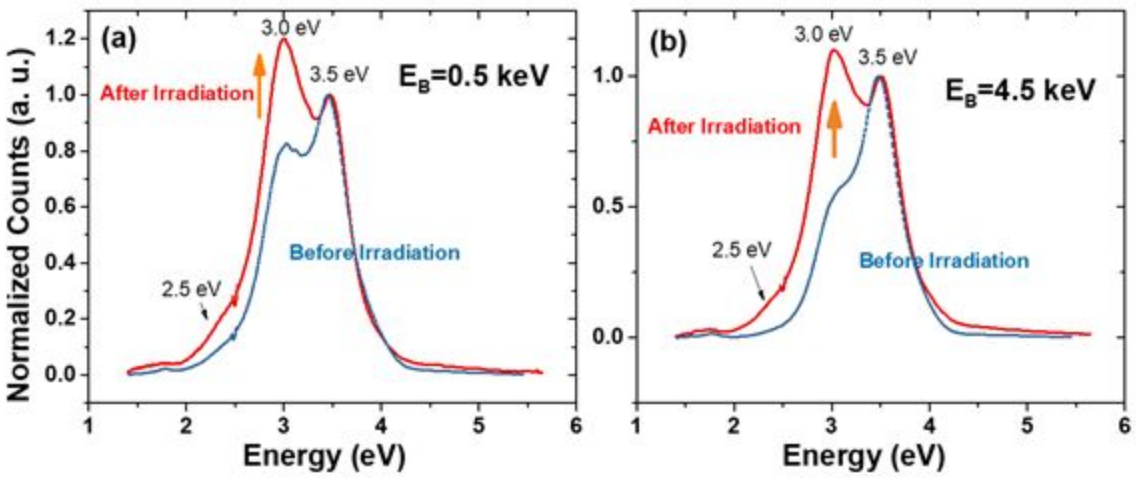

Figure 10: CL Spectra before and after neutron irradiation at beam energies 0.5 eV(left) and 5 eV(right)

Once again, a depth profile was created, and is shown below.

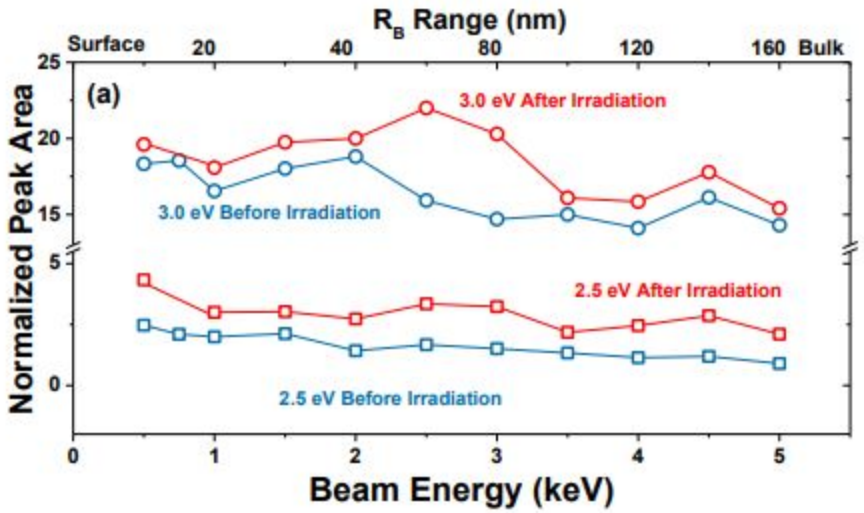

Figure 11: Depth Profile for LPCVD gallium oxide pre and post neutron irradiation

The irradiation treatment has increased the intensities of the peaks of both the 3.0eV and 2.5 eV peak. In addition, there is not as clear of a depth dependency with this treatment, which is consistent with expectations as neutron irradiation is typically a process that penetrates through the sample. The increase in peak intensities by almost 20% indicates that these features are related to gallium related vacancies.

Further studies with more radiation have shown promising results as well.

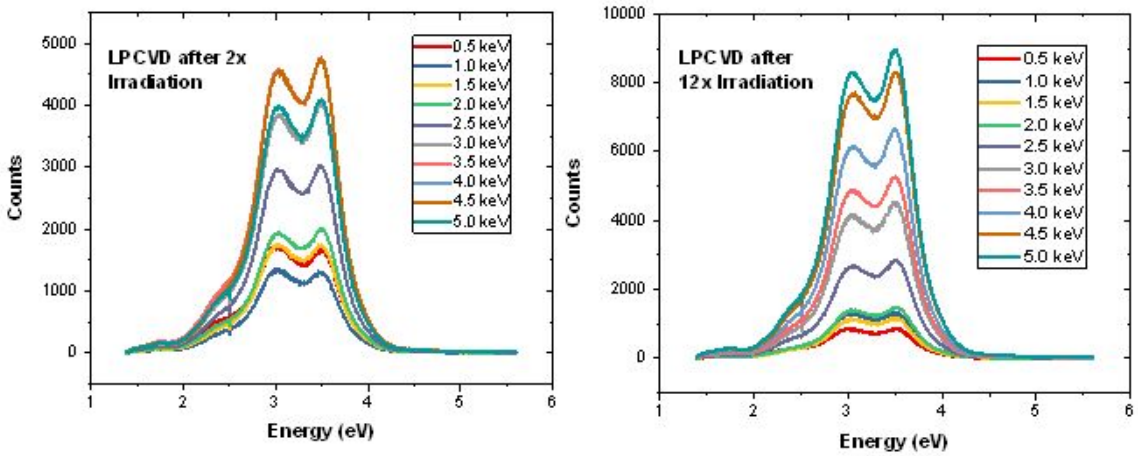

Figure 12: DRCL spectra with further irradiation

The spectra with further irradiation shows systematic increase in the intensity of the 2.5eV and 3.0 eV features, while the 3.5 eV feature remains relatively constant. Depth profiles created from these peaks areas show that both the 2.5 eV peak and the 3.0 eV peak show systematic increases after each dose of irradiation, while the effect on the 3.5eV oxygen vacancy related peak is less obvious.

SPS and Transient SPS Measurements

SPS was also used to confirm the defect features observed in DRCLS. SPS taken on MBE-grown gallium oxide has shown the transitions found through other methods.

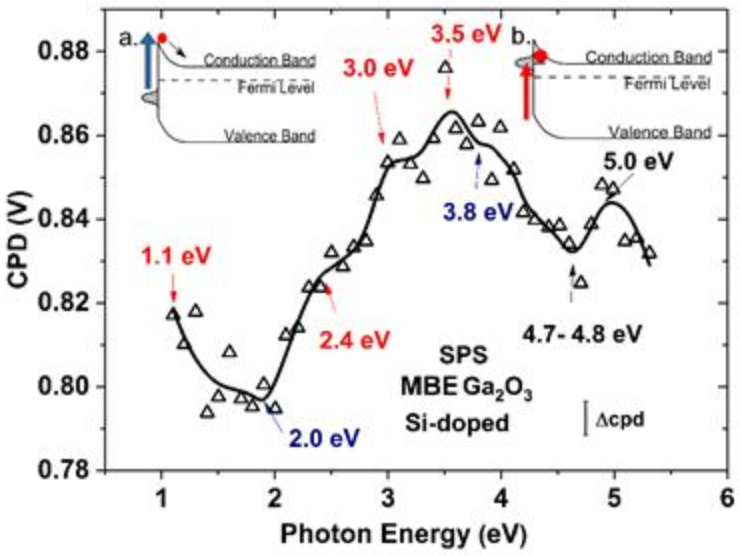

Figure 13: SPS spectrum of MBE grown gallium oxide

The spectra above shows transitions and slope changes corresponding to the peak levels previously identified, specifically at 2.5 eV. 3.0 eV, and 3.5 eV.

Transient SPS was also used to estimate the approximate density of defect states in this material. Below are two transient SPS results for the 3.0 and 3.5 eV defect features.

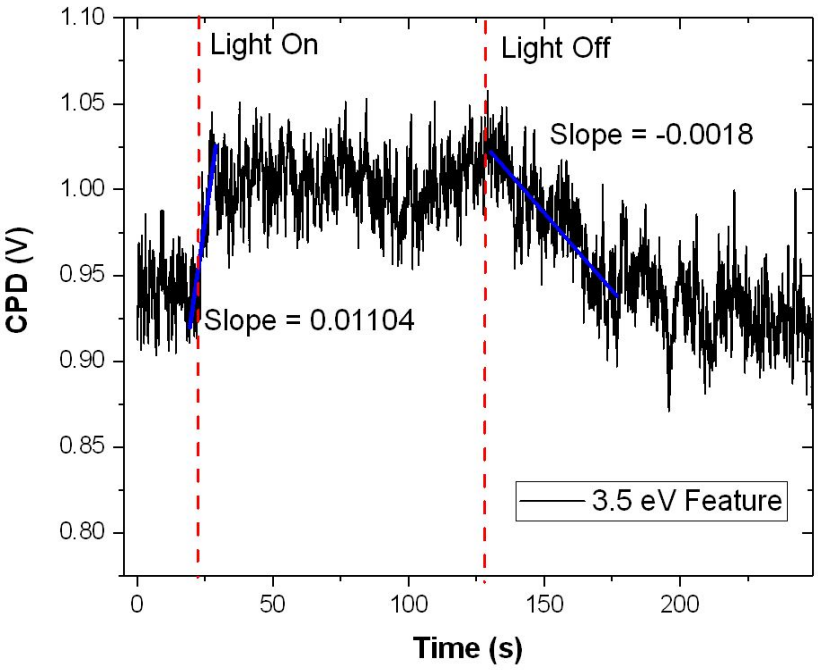

Figure 14: Transient SPS spectra for 3.5eV feature

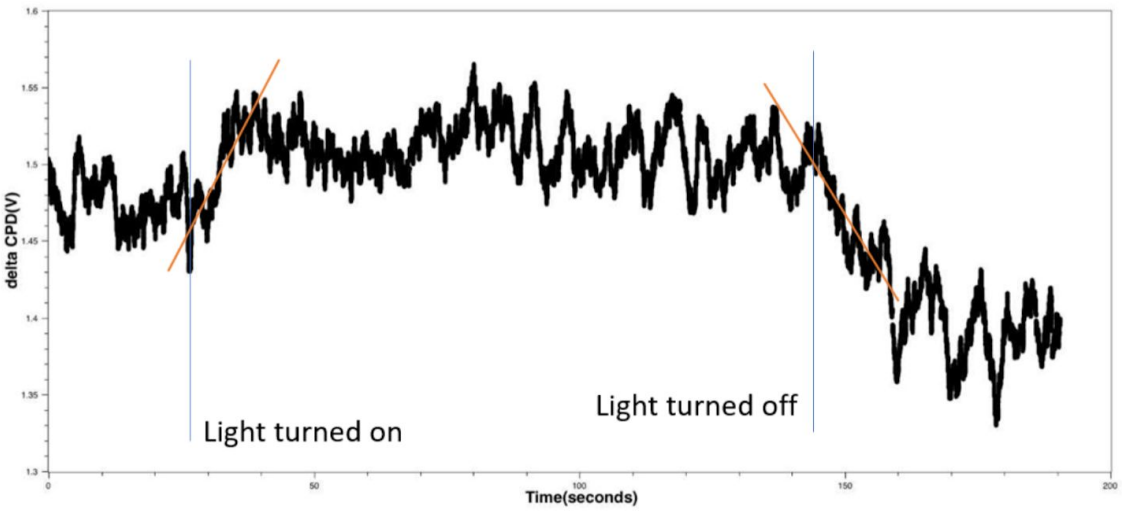

Figure 15: Transient SPS Spectra for 3.0 eV feature

These spectra allow us to gain baseline defect concentrations for each of these features. The 3.5 eV scan corresponds to a defect concentration of 1.55E11 cm^{-2}, and the 3.0eV scan corresponds to a defect concentration of 1.86E9 cm^{-2}. Both of these concentrations agree, within the same order of magnitude, with results from an paper measuring these defect states through an alternate method, Deep-Level Transient Spectroscopy. This will be further useful when transient SPS is used to look at samples treated with ROP and irradiation, as this can confirm the trends shown in the depth profiles obtained from DRCLS.

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

Gallium Oxide is a material with great potential due to its high bandgap and relative availability and ease of production. The work currently being done at the Ohio State EMNL lab is critical to the development of Ga_2O_3 as a widespread material, as understanding the nature of defects is important to device construction and performance. DRCLS, SPS, and tSPS can be used in conjunction to understand the underlying properties of the material. This work has identified

the possible nature of defects, and future work will allow us to further understand how to improve devices made out of gallium oxide.

Future work includes further tSPS measurement on these samples. Currently, the measurement is highly susceptible to noise, and the fact that gallium oxide has a high bandgap and is insulating does not lead to a reliable measurement. Depositing contacts onto the material may yield higher success with the measurement, and allow us to better understand the densities of each of the defect states identified. Furthermore, work is being done with greater doses of neutron irradiation, and this work will allow us to better understand the nature of the gallium related vacancies.

References

[1] Tippins H. H. 1965 Phys. Rev. 140 A316

[2] H. Gao, S. Muralidharan, N. Pronin, M. Karim, S. M. White, T. Asel, G. Foster, S. Krishnamoorthy, S. Rajan, L. Cao, M. Higashiwaki, H. von Wenckstern, M. Grundmann, H. Zhao, D. C. Look, and L. J. Brillson, "Optical signatures of deep level defects in Ga2O3," Appl. Phys. Lett. 112, 242102 (2018).

[3]L. J. Brillson, "Cathodoluminescence spectroscopy of metal–semiconductor interface structures," J. Vac. Sci. Technol., A 6, 1437 (1988)

[4]H. C. Gatos and J. Lagowski, "Surface photovoltage spectroscopy—A new approach to the study of high-gap semiconductor surfaces," J. Vac. Sci. Technol. 10, 130 (1973)

[5]D. Turkoglu, J. Burke, R. Lewandowski, and L. R. Cao, "Characterization of a new external neutron beam facility at the Ohio State University," J. Radioanal. Nucl. Chem. 291, 321 (2012)